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Abstract

URANIUM DIOXIDE PRODUCTION. A SURVEY OF ELECTROCHEMICAL REDUCTION AND PRECIPITATION FROM CARBONATE SOLUTIONS

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Conditions for the electrochemical reduction of uranium(VI) in carbonate solutions to uranium(IV), and conditions for the subsequent precipitation of uranium dioxide (or hydrated oxides) are given and the obtained results discussed.

The electrochemical reduction of uranium(VI) in carbonate solutions proceeds by one-electron-step reaction to uranium(V) carbonate complex, which subsequently dismutates to uranium(VI) and uranium(IV) carbonate complexes by a second order kinetics. The dismutation rate depends on pH and on the total carbonate concentration. The constant potential electrochemical reduction on the mercury electrode seems to be the only possible way to obtain stable uranium(IV) carbonate complex solutions. The reduction of uranium(VI) on platinum and nickel electrodes was not selective. Therefore, these metals could not be used as electrode materials in the reduction process.

The conditions for the precipitation of uranium(IV) from stable solutions are described. The precipitation is induced either by raising the temperature to 60°C, or by raising the pH of the solution, or by dilution. Concentration limits of the precipitation are shown by plotting the concentration of total sodium carbonate vs. concentration of uranium.

The reduction of uranium(VI) on mercury cathodes of different areas (1 : 10 : 100) was carried out. The current density on the cathode depends on the rate of stirring at given experimental

conditions. In order to obtain the optimal current densities a pilot-plant electrolysis cell with a rotating mercury electrode was constructed. The cell had an operating volume of 200 liters. The cathode potential was electronically controlled.

On the basis of the results obtained, the flow sheet of a cyclic process is proposed. Two aspects of application are discussed.

1. Production of uranium dioxide from ammonium diuranate by electrolysis of ammonium carbonate solutions of high uranium content;
2. Extraction of uranium from ore leach liquors to obtain technical concentrates. Application to low grade ore leach solutions is considered also.

The precipitate, obtained from solutions of high uranium concentrations, shows regularly an O/U ratio lower than 2.10. After drying at 300°C, in inert atmosphere, the products had cubic crystal structures determined by X-ray analysis.

The pellet of uranium dioxide pressed at 4000 kg/cm^2 and sintered at 1350°C had densities up to 10.2 g/cm^3.